This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

M.H

GB 99/3116

The Patent Office

PCT/GB 99/03116

REC'D 25 OCT 1999
WIPO PCT

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

4

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed R. Mahoney

Dated 15 OCT 1999

Patents Form 1/77

Patents A 77
(Rule 16)

The Patent Office

1/77

18SEP98 E390826-1 D01554
P01/7700 25.00 9820214.6

The Patent Office

Cardiff Road
Newport
South Wales NP9 1RH

Request for grant of a patent

(See t on the back of this form. You can also get an ex leaflet from the Patent Office to help you fill is form)

THE PATENT OFFICE
17 SEP 1998
NEWPORT

1. Your reference — RK590 GB1

2. Patent application number *(The Patent Office will fill in this part)* — **9820214.6** — 17 SEP 1998

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

RAYCHEM LIMITED
PATENT DEPARTMENT
FARADAY ROAD, DORCAN
SWINDON SN3 5HH
UNITED KINGDOM

Patents ADP number *(if you know it)* — **8052002**

If the applicant is a corporate body, give the country/state of its incorporation — UNITED KINGDOM

4. Title of the invention — **BONDING POLYMER INTERFACE**

5. Name of your agent *(if you have one)*
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Anthony William JAY
RAYCHEM LIMITED
European IPLD
Faraday Road, Dorcan, Swindon
Wiltshire, SN3 5HH,
United Kingdom.

Patents ADP number *(if you know it)* — **23655002**

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. ~~If this application is divided or~~ otherwise derived from an earlier UK application give the number and the filing date of the earlier application

Priority application number *(if you know it)*	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? — YES
(Answer 'Yes' if:
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	6
Claims(s)	2
Abstract	-
Drawing(s)	-

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	FEE SHEET

11. I/We request the grant of a patent on the basis of this application.

Signature Date 17 September 1998

ANTHONY WILLIAM JAY

12. Name and daytime telephone number of person to contact in the United Kingdom SHIRLEY NOTT 01793 572120

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.

b) Write your answers in capital letters using black ink or you may type them.

c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.

d) If you have ansered 'Yes' Patents Form 7/77 will need to be filed.

e) Once you have filled in the form you must remember to sign and date it.

f) For details of the fee and ways to pay please contact the Patent Office.

BONDING POLYMER INTERFACE

This invention relates to insulation for electrical wire or cable (hereinafter "wire") in which a strong bond is achieved at an interface between a layer of polyolefin-based material and a layer of fluoropolymer-based material. The invention is especially useful in multi-layer insulation of electrical wires, where it is notoriously difficult to achieve high-performance bonding between layers of such materials while retaining an acceptable balance in the complex relationships of other wire performance requirements, which are specialised and different from the criteria for other kinds of article such as mouldings or packaging films.

The conventional approach to the bonding of polyolefins and fluoropolymers is to employ a tie layer (e.g. US patent 5,589,028). Tie layer materials tend to be expensive, may compromise other properties, e.g. heat ageing, and add complexity to the manufacturing process in forming the extra layer. They may also be of limited effectiveness in terms of the bond strength developed.

In the wire insulation according to the present invention, a high bond strength is unexpectedly achieved by a combination of the formulation of the polyolefin layer; the choice of the fluoropolymer material; and a cross-linking reaction, preferably effected by the application of radiation, especially ionising radiation.

The invention accordingly provides an electrical wire having insulation comprising comprising

(i) at least a first layer of a material comprising at least 20%, preferably at least 40%, more preferably at least 60% or at least 80%, by weight (of the whole material composition) of a carbonyl-containing polymer (homopolymer or copolymer or terpolymer) having a non-aromatic backbone, of which polymer the or at least one constituent monomer is a carboxylic acid ester or salt, preferably an acetate or acrylate, especially vinyl acetate, or methyl acrylate, or butyl acrylate, the said monomer itself constituting at least 5%, preferably at least 9%, more preferably at least 15%, by weight

of the said co-, or ter- polymer when used and the remainder of the said co-, or ter-polymer preferably being derived from olefinic monomer, preferably ethylene;

in contact with

(ii) at least a second layer of a material comprising a partially fluorinated polymer, preferably containing at least 10%, more preferably at least 50%, or at least 90%, by weight of polyvinylidene fluoride (PVDF), or especially preferably a copolymer based on VDF with a partially or fully fluoroinated co-monomer, most preferably a copolymer of VDF and hexafluoropropylene (HFP);

wherein the said layers (i) and (ii) whilst in contact with each other have been subjected to cross-linking reaction, preferably by radiation, more preferably ionising radiation, sufficient to increase the peel bond strength between the said layers to at least 5N, preferably increasing the bond strength by at least 50%, more preferably by at least 100%, especially by at least 500% or 1000%, compared to that between the uncrosslinked layers.

Advantages of achieving a strong bond in accordance with this invention include:

- abrasion resistance of a surface layer can increase if it is bonded to a substrate material;
- improved resistance to peel, especially if one of the layers is damaged/perforated;
- improved resistance to blistering of the two layers, if heat is applied;
- improved resistance to delamination/creasing/wrinkling between the two layers, e.g. due to mechanical stress or chemical exposure e.g. to solvents.
- achievement of reduced wire bend wrinkling while maintaining adequate cut-through and notch propagation resistance, the latter being unexpected since strongly adherent layers would normally be expected fairly easily to transmit a cut or notch in the outer layer through to the inner layer.

The **bond strength** described in this application can most conveniently be measured in terms of peel strength between bonded strips of the two materials in question. A standard method which can be used for such a test is ASTM 1876-95. By this definition, a significant bond could be one for which the peel force exceeds 5N, and a strong bond one of peel force greater than 10N.

The polyolefin-based layer (i) comprises at least 20%, preferably at least 40%, more preferably at least 60% or 80%, by weight of the said carbonyl-containing polymer. The rest of the formulation may be whatever is required in the way of polymers and additives such as anti-oxidants, pigments, fillers, flame retardants, etc, as known per se, to give the required mechanical, thermal, electrical etc. properties to the polymer. The carbonyl-containing polymer may include alternating olefin/carbon monoxide copolymers (for example those available under the Trade Mark "Carilon" from Shell), or ionomers (for example those available under the Traed Mark "Surlyn" from du Pont).

The fluoropolymer-based layer (ii) also may contain other additives as known per se to give it required properties in addition to bonding. In addition to the preferred polymers indicated above, the partially fluoroinated polymer may be selected from ethylene/tetrafluoroethylene copolymers (e.g. "Tefzel" Trade Mark) and ethylene/chlorotrifluoroethylene copolymers (e.g. "Halar" Trade Mark).

Methods of fabricating the wire may include any process which causes intimate contact between the above mentioned polyolefin and fluoropolymer-based formulations. Examples include coating of one material onto a pre-formed layer of the other, dual or multi-walled extrusion to form insulation layers respectively containing one or other of the aforementioned two classes of material. The olefin-based material (i) is preferably the inner layer and the fluoropolymer-based layer (ii) preferably the outer layer on the wire. The layers made from the two different materials could be coextruded, tandem extruded, multipass extruded, sprayed, coated or vapour deposited. Known wire insulation processes such as tube draw-down extrusion may be used, to form one or more of the layers, but pressure extrusion as known per se is preferred for optimum adhesion of the second and any subsequent insulation layers to be applied to a pre-formed underlying layer.

The insulation on the wire is exposed to cross-linking reaction, which may involve chemical reagents such as peroxides, but preferably is effected by radiation, especially from a source of ionising radiation capable of causing the formation of free radicals and

thus, it is believed, cross-links, in the polymers, some of which should preferably be formed in the region of the interface between the two materials. Penetration of radiation into the material at least as far as the interface is therefore desirable, although not necessarily essential if ion or radical mobility, for example, enables molecular reactions to continue at or near the interface after the radiation process. The radiation source could, for example, be a radioisotope, or an X-ray source, or possibly a non-ionising radical-generating source, for example a UV source, but is preferably an electron beam, more preferably one providing a beam dose greater than 2 Mrads, preferably at least 10 Mrads, more preferably at least 15 Mrads, into the material.

It has been found that enhancements to the interfacial bond strength may be obtained by using certain additives and/or by heating after the radiation process.

Additives preferably include a cross-linking promoter ("pro-rad") in the polyolefin-based material and/or in the fluoropolymer-based material. Known cross-linking materials may be used, preferably methacrylate/acrylate based ones, and very preferably, those of the type trimethylolpropanetrimethacrylate (TMPTM), in the polyolefin material and/or in the fluoropolymer material.

The **application of heat** to the wire during or after the crosslinking process can significantly increase the bond strength. This should preferably be to a temperature of at least 40°C for at least 20 seconds, more preferably at least 50°C for at least 30 seconds, and very preferably at least 60°C for at least 60 seconds. The heat treatment should preferably be applied soon after the cross-linking, for example within one day, or more preferably within 4 hours, or even immediately.

Experimental results:

All results quoted in the Tables below were obtained by testing pressed plaques of the two materials prepared by the usual polymer handling techniques, well known per se. The plaques were pressed together to bond them face-to-face and the bonded assembly was irradiated as indicated.

Effect of Radiation Dose (from an electron beam with 1.5MeV accelerating voltage)

Material 1	**Material 2**	**Dose(Mrad)**	**Peel (N)**
Ethylene/Vinyl Acetate Copolymer (Elvax 3190G Trade Mark) of 25wt% VA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	0	0.5
Same as above	Same as above	15	40

Effect of % MA Co-monomer in Olefinic Material

Plaques of 100% EMA copolymer, pressed together with plaques of above Material 2.

% MA in EMA	**Copolymer grade**	**Dose(Mrad)**	**Peel (N)**
7	Lotryl* 9MA02	20	4
28	Lotryl* 28MA02	20	45

*Lotryl is a Trade Mark.

Effect of % Copolymer in Olefinic Material

Plaques listed below are mixture of HDPE with given % of EEA copolymer (Borealis LE 5861, ethylene/ethyl acrylate itself containing 15% EA), pressed together with plaques of above Material 2.

% EEA	Dose (Mrad)	Peel force (N)
0	20	0
80	20	70

Effect of Pro-rad in polyolefin material

Plaques listed below are mixture of HDPE with 80% of above EEA copolymer plus given % of known cross-linking agent (Sartomer SR350DD Trade Mark), pressed together with plaques of above Material 2.

% Pro-rad	**Dose (Mrad)**	**Peel force (N)**
0	20	70
4	20	>130

Effect of heat applied after electron beam irradiation

Plaques listed below are mixture of HDPE with above EEA copolymer in the weight ratio 2:8, plus a range of other additives as known per se at a total additive level of 24wt%, pressed together with plaques of above Material 2 and irradiated in a 1.5MeV electron beam to a dose of 20 Mrads. One of the plaques was heated at a temperature of 60°C for 60 seconds, while the other plaque, being a control, was kept at room temperature. The plaques were subsequently peel tested at room temperature.

Sample	Beam dose (Mrad)	Peel force (N)
Control	20	9
Heated	20	15

EXAMPLE OF WIRE CONSTRUCTION

An electrical wire in which the insulation consists of two polymeric layers bonded together according to the present invention may be made as follows.

The inner layer of insulation (i.e. nearer to the wire conductor) is a polyolefin-based material, consisting predominantly of (a) an EEA copolymer containing 15wt% EA and (b) HDPE in a weight ratio of approximately 8:2 copolymer:HDPE, with usual other additives present in smaller proportions including crosslinking promoters, stabilisers, antioxidants, pigments and process aids at a total level of 24wt%. This layer is pressure extruded or draw-down-tube extruded onto the metallic conductor. The outer layer of insulation consists predominantly of a PVDF/HFP copolymer containing 10wt% HFP (Kynar 3120-50 Trade Mark), which in this example contains a crosslinking promoter, and other known additives such as pigments, plasticisers, stabilisers, antioxidants and process aids in usual proportions totalling 7.5wt%. This outer layer is either pressure extruded in a separate operation onto the pre-formed inner layer, or extruded together with the inner layer in a single operation by a tandem or co-extrusion process.

This coated wire product is then passed through an electron beam, and receives a radiation dose in the range 5-30 Mrad. Heat treatment as aforesaid may follow.

Claims

1. An electrical wire or cable having insulation comprising
(i) at least a first layer of a material comprising at least 20%, [preferably at least 40%, more preferably at least 60% or at least 80%,] by weight of the whole material composition of a carbonyl-containing polymer (homopolymer or copolymer or terpolymer) having a non-aromatic backbone, of which polymer the or at least one constituent monomer is a carboxylic acid ester or salt, [preferably an acetate or acrylate, especially vinyl acetate, or methyl acrylate, or butyl acrylate,] the said monomer itself constituting at least 5%, [preferably at least 9%, more preferably at least 15%,] by weight of the said co- or ter- polymer when used and the remainder of the said co- or ter-polymer preferably being derived from olefinic monomer, [preferably ethylene];
in contact with
(ii) at least a second layer of a material comprising a partially fluorinated polymer, [preferably containing at least 10%, more preferably at least 50%, or at least 90%, by weight of polyvinylidene fluoride (PVDF), or especially preferably a copolymer based on VDF with a partially or fully fluorinated co-monomer, most preferably a copolymer of VDF and hexafluoropropylene (HFP)];

wherein the said layers (i) and (ii) whilst in contact with each other have been subjected to cross-linking reaction, [preferably by radiation, more preferably ionising radiation,] sufficient to increase the peel bond strength between the said parts to at least 5N, [preferably increasing the bond strength by at least 50%, more preferably by at least 100%, especially by at least 500% or 1000%, compared to that of the uncrosslinked parts].

2. A wire or cable according to claim 1, comprising multiple alternating layers of the materials constituting the said layers (i) and (ii).

3. A wire or cable according to claim 1 or 2, which contains at least one crosslinking promoter in the material of either or both of the said parts (i) and (ii), [preferably an

ester-based, more preferably a methacrylate/acrylate based, promoter, especially of the TMPTM type].

4. A wire or cable according to any of the preceding claims which has been subjected after the said ionising radiation to heat treatment, [preferably at a temperature of at least 40°C for at least 20 seconds, more preferably at least 50°C for at least 30 seconds, and very preferably at least 60°C for at least 60 seconds].

5. A method of making a wire or cable according to any of the preceding claims, comprising the steps of providing thereon the said layers (i) and (ii) in contact with each other, and subjecting the said layers while in contact with each other to the said cross-linking, [preferably by ionising radiation].

6. A method according to claim 5, including the further step of subjecting the wire or cable after the said radiation to heating, [preferably at a temperature of at least 40°C for at least 20 seconds, more preferably at least 50°C for at least 30 seconds, and very preferably at least 60°C for at least 60 seconds].

****

PCT/GB99/03116

Raychem Ltd.

20/9/99.